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The Synthesis and Characterization of PANI - CuPc Organic Semiconductor Hybrid Material

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Abstract

CuPc was synthesized with 4-Nitrophthalonitrile and p-Cresol as the source materials of benzene ring by the template synthesis method of two steps reaction. With aniline as the source material of polyaniline, using chemical oxidative polymerization method of one-step reaction, through doping with perchloric acid, vitriol and nitric acid obtained semiconducting doped PANI. On this basis, selected the intermediate substance of reactive process, by means of molecular hybrid modification polymerized the two substances to form a kind of new organic semiconductor material CuPcxPANI1-x. Through the analysis of characterization means such as mass-spectrometry, infrared absorption spectroscopyand thermogravimetry, the results indicated that molecular weight of the phthalocyanin molecular fragment was confirmed as 234 through the analysis of mass-spectrometry, and the theoretical value of phthalocyanin was 234.34, which validated that the synthesis process of the phthalocyanin molecular fragment was right. Through the analysis of thermogravimetry, the new substance from hybrid synthesis forming thin film was viable using the technology of evaporation.

Keywords: CuPc, PANI, organic hybrid synthesis, characterization synthesis

1. Introduction

Among the organic semiconductor materials, polyaniline(PANⅠ) and metal phthalocyanine are the typical ones. Polyaniline is an obvious one-dimensional chain polymer, with highly stable geometry, which has the electrical properties just only in the condition of doping. While metal phthalocyanine(MPc) is the typical ligand conjugate complex plane, conductive mechanism follows the one-dimensional chain of conductive properties of conjugated polymers[1-4].

By means of the technology of characterization as mass spectrometry, infrared spectroscopy, differential thermal gravimetric, the best process and property of final product were made, to establish the reaction mechanism model.

2. Experiment

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A. Synthesis of polyaniline

Aniline as the source material was used in this paper, one-step reaction of the chemical oxidation polymerization[5], to carry out the synthesis of polyaniline. 9.4mL analytical grade aniline and 200mL1.5mol / L hydrochloric acid after the second vacuum distillation mixed in a three necked round-bottom flask，continuously reacted with 10 ~ 15g ammonium persulfate and 1.5mol/L hydrochloric acid solution in the condition of sub-zero about 5-6 hours. When the solution became dark green, filtered, washed with 1.5mol / L hydrochloric acid and distilled water. After acetone extraction, dried in the vacuum oven at 80 ℃ for 10h. At last got active eigenstate PANI, dealing with 8% (wt) NH4ON until 24h.

Under magnetic stirring about 4hours, amount of active PANI was added to a certain amount of 2mol / L HClO4 (or H2SO4, or H3NO3), then washed with distilled water and acetone, after the vacuum drying to get the doped $HClO_4$（H_2SO_4 or HNO_3）PANI.

B. Synthesis of CuPc

5~7g cresol and 3 ~ 5g 4 - nitro-phthalonitrile mechanical mixed with 40 ~ 60mlDMF (N-N dimethyl formamide). During this time, every 1h, added 2 ~ 3g potassium carbonate, totally about 5 times, which played a role of catalytic. When the solution gradually turned from yellow to red, 24 hours after this phenomenon, filtered out the insoluble salt. The filtrate was dripped in 100ml distilled water, stirred 1h, filtrated, and washed to neutral. Wetting with a small amount of methanol, and then recrystallized three times in the use of methanol, vacuum dried 12h to get the white which was molecular fragments of Phthalocyanine.

2~3g intermediate product was brought to 30 ~ 40ml pentanol stirred with 0.1 ~ 0.3g copper chloride about 10min, dropping 2~3ml DBU, turned to dark green. The heating was carried on for 5h, under the protection of N_2, using 250ml 1mol / L hydrochloric washed to acid and water to neutral. 60 ℃ methanol washing, Methanol extraction 24h, and then Chloroform 48h, Vacuum drying to get the CuPc.($C_{60}H_{40}N_8O_4Cu$).

C. Hybrid Modify

On the base of synthesizing single material CuPc and PANI, Polymerizated to form a new organic semiconductor material, on the method of molecular hybridization modify, as followed: synthesizing intermediates. （1）Premise in phthalocyanine molecule, adding 30 ~ 50ml pentanol and 0.2 ~ 0.4g copper chloride to stirred 9 ~ 11min, and then mixing 2~3ml DBU. When it turned to dark green, reacted 4.5~5.5h in the protection of N_2, on 145~155℃. 240 ~ 260ml 1mol / L hydrochloric acid to wash, then wash to the neutral. Washed with 50 ~ 60 ℃ methanol, filtered, methanol extracted 23 ~ 25h, adding 200 ~ 500ml chloroform to extracted 45 ~ 50h to prepare the intermediate CuPc. According to the aforementioned method got the intermediates Polyaniline. (2) Mixed hybrid. Put amount of the two stand-intermediate materials into the organic reactions vessel, in accordance with the x value corresponds to the ratio (x is weight ratio coefficient 0.01~0.99), magnetic stirring, adding acid anions dissolved in chloroform about 3 ~ 5 h, crystallizated with distilled water and acetone, Vacuum dried to get the sensitive material, CuPcxPANI1-x.

3. Results and discussion

In the course of chemical synthesis, factors that affected the purity including the ratio of raw materials and the purity、synthesis temperature、 reaction time and the stirring speed. The yield of phthalocyanine molecular fragment was about 50%, and CuPc was 9%. Synthetic products were identified by mass spectrometry. Spectrum analysis showed that the phthalocyanine molecular fragment's molecular weight which determined by mass spectrometry was 234 (theoretical value is 234.34) as apparent in Fig.1. It proved the correctness of the synthesis of the phthalocyanine molecular fragment. From the mass spectrometry analysis also found that there were many different by-product which was one of the reasons for the low yield of the end products.

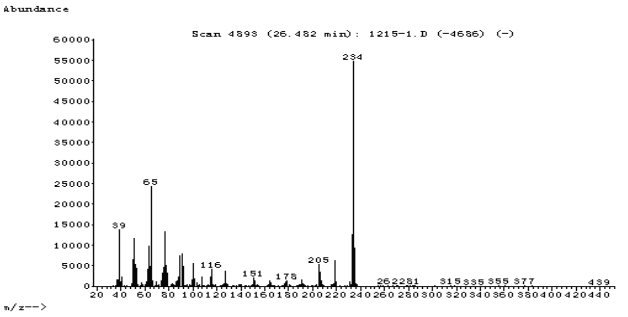

Fig. 1 Mass spectrogram of the phthalocyanine molecular fragment

The difference of infrared absorption peaks was changing with the stretching vibration of chemical bonds in the material elements, which determined the basic structure and composition of synthetic substances and inferred the correctness of the end synthesis product of the process routes.

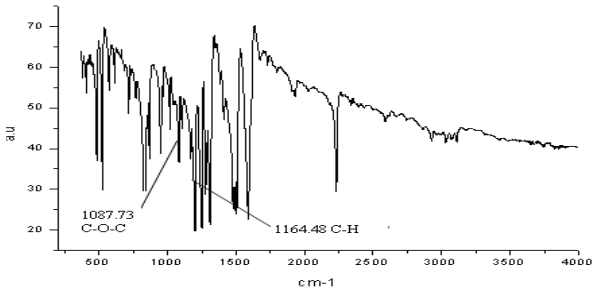

Fig. 2 Infrared absorption spectrogram of the phthalocyanine molecular fragment

The infrared absorption spectrogram of the phthalocyanine molecular fragment was illustrated in Fig.2.

Molecular Orbital Theory of Organic[6]: Spectrum of conjugated organic molecules is from the large benzene rings π - π * transition. Conjugated molecules in the visible region own two main absorption bands, one is the 600-800nm Q-band [la_{lu}-(π)- le_g(π*)]and the other is the 200-400 nm B-band (which also can be called soret band) [la_{2u}(π)-le_g(π*)], in addition to several relative strong UV absorption, including the transition from the lower level π orbital to le_g (π*)orbital of and electron on N to le_g (π*) orbital .

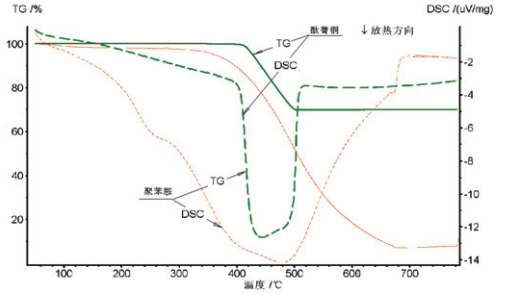

Fig.3 The themogravimetic curve of CuPc and PANI

The themogravimetic curve of CuPc and PANI as shown in Fig.3, which illustrated that CuPc at 430 ~ 440℃ started the first weightlessness, and the process was releasing heat from the beginning to the end, the

tropical place appeared in 400 ~ 500℃. It demonstrated that it may be reference with the degree of integration elements, location and type of the central metal and so on. PANI began to lose weight slowly from 300℃. Compared with the weightlessness of CuPc, the weightlessness of PANI all showed the phenomenon of slow weight lossing. It proved that the binding and cohesion of PANI molecular were close firmly. All the decomposition process were accompanied the releasing of heat.

Fig.4 was the themogravimetic curve of CuPc - PANI doped with perchloric acid from which can be seen that only a slight weight losed trend appeared at 550 ℃ in the range of 25 ~ 800℃. It meant that materials had the phenomenon of sublimation on this temperature. However, there was only 10% weight loss at 800℃, which showed the new materials only lose surface impurity and a small amount of functional groups, which could not be completely decomposed, proved the new materials had strong binding force. When the decomposition temperature was above 800 ℃, all the decomposition process was accompanied by the release of heat, which was a slow exothermic process. The lowest exothermic temperature corresponded to sublimation temperature point. Therefore, the mixed-hybrid coating process of metal phthalocyanine and polyaniline and its new materials by evaporation was feasible.

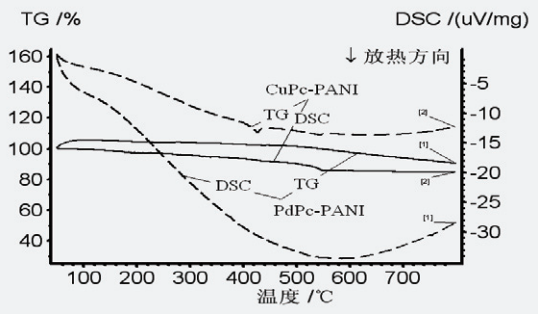

Fig.4 The themogravimetic curve of CuPc - PANI doped with perchloric acid

4. Conclusion

By two-step reaction of 4 - nitro-phthalonitrile and phenyl methyl phenol as the source materials of the template was synthesized CuPc; By one-step reaction process, aniline as the source material of the chemical oxidation polymerization synthesized polyaniline. The doped PANI conductivity was controlled by perchloric acid, sulfuric, and nitric acid; As the two kinds of substances in the above synthesis method, based on the process of selecting the intermediate reaction materials, two polymer formed a new organic semiconductor materials CuPcxPANI1-x by the method of molecular hybrid modification; Using mass spectrometry to determine the product of intermediate material - phthalocyanine molecular fragments weight 234 consistent with the theoretical value 234.34, which verified the correctness of the synthesis process; Infrared absorption analysis to determine the peak absorption of phthalocyanine fragments was consisted with literature values peak, which also testified correctness of the synthesis process in the second step; Thermal gravimetric analysis showed that the new material was a slight trend in weight loss in the sublimation temperature of 550 ℃, rather than decomposition. The phenomenon showed the new material had strong binging force. The higher decomposited temperature above 800 ℃, accompanied with a slow exothermic process , benefited the control of material forming conditions.

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